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A technique to determine the lifetime of induced luminescence in subnanosecond time frames has been developed. The excitation source is a picosecond Q-switched Nd glass or Ruby laser with a frequency multiplier. The luminescence intensity profile of a single pulse is photographically recorded from an oscilloscope trace. A convolution technique is applied to analyze the traces with the use of a computer program, NLCON. The program gives values of lifetime as a function of root mean squares and produces the plots of the observed and calculated luminescence profiles.

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PREFACE

Excited state decay time measurements of materials relevant to our laboratory mission are essential when considering laser interaction with systems. Our studies have shown that many materials have decay times in the nanosecond and sub-nanosecond time frame. Consequently, we have developed a technique using picosecond laser sources and computer analysis, that, combined, give us a method to effectively resolve lifetimes as short as 50 picoseconds. This report deals with a brief history of lifetime measurements, explains our method of measurement, and presents a sample case.

We wish to acknowledge the contributions of Dr. John A. Sousa, on whose original work this study is based. His suggestions and encouragement have been very helpful in the accomplishment of this task.

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MEASUREMENT OF NANOSECOND AND SUB-NANOSECOND LIFETIMES

Introduction

This laboratory has comprehensively studied the interaction between laser light and material systems. Particular emphasis has been placed on analyzing the resulting induced luminescence with spectrographic type instrumentation, in an effort to detect and identify the emitting species. This kind of information is necessary in the design of camouflage systems against the threat of laser surveillance. To complete the study of induced luminescence, its decay time must also be considered, for the understanding of camouflage techniques requires a knowledge of the fundamental relaxation processes involved. For this study, we assume that decay times (fluorescence) can be described by a single exponential decay of an excited molecule to its ground state. The lifetime of the excited state is the time it takes for light to be emitted as fluorescence and is characterized by the time required for the concentration of excited molecules to decrease to 1/e of its original value. ($1/e \simeq 1/2.718 = 0.368$). Until recently, normal lifetime measurements (10^{-8} to 10^{-9} second) have been determined by indirect methods due to the unvailability of short excitation pulses. When Q-switched lasers became available (pulses $\sim 10^{-9}$ sec) the emphasis then shifted to making direct measurements[1], and now picosecond lasers have extended the accurate measurement of lifetimes to subnanosecond time frames. In these times, the detection system restricts direct measurements, and novel techniques have to be developed to extract lifetimes from undesirable perturbations. This study describes a method by which the excited state decay times (fluorescence), from nanoseconds to picoseconds, can be determined using single pulse excitation sources.

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[1]R.A. Kashnow and J.A. Sousa, J. Applied Physics, 42. No. 5. April 1971.

Equipment

For the excitation source, we use a single pulse extracted from a mode-locked laser pulse train. See Figure 1. Each pulse is $\sim$ 10 psecs. FWHM, as measured by two photon fluorescence techniques, and the pulses are spaced 8 nsecs apart. The extracted pulse is subsequently amplified and changed in wavelength by various doublers. Table 1 shows the

A B

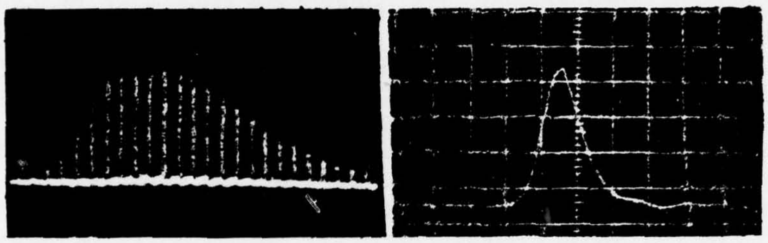

FIG. 1. A) LASER MODE-LOCKED PULSE TRAIN. HORIZONTAL SWEEP 20 ns/div. B) SINGLE PULSE SELECTED FROM A MODE-LOCKED PULSE TRAIN. HORIZONTAL SWEEP 1 ns/div.

energies and wavelengths available from our laser system. For most of the work, we used Nd doubled to 530 nm.

TABLE 1: Energy and Wavelengths Available from the Laser System

Laser	(nm)	Energy (Train)	Energy (Pulse)
Nd	1060	1.00 J	40 mj
	530	.10	8
	353	.03	
	265	.01	
Ruby	694	.40	
	347	.06	

The detector is a PIN Photodiode (H.P. 4220) specially integrated into a mount to reduce its response time to a few hundred picoseconds.

It is coupled through a 1/4-meter monochromator to a 7904 Tektronix oscilloscope. The monochromator is used to filter out the laser light and provide spectral scanning for wavelength dependent phenomena. A schematic representation of our total excitation and detection system is shown in Figure 2. Data are generated in the following way: The laser pulse sample interaction causes the sample to fluoresce. The monochromator, which is tuned to the wavelength of fluorescence, allows the signal to come through, but discriminates against the laser light. A voltage pulse from the PIN photodiode, descriptive of the fluorescence intensity, is displayed in time on the oscilloscope and the resulting trace photographed. In addition to the fluorescence pulse, a trace of the laser pulse is also photographed, and these data together are processed to determine the lifetime of the decay.

This system provides us with a way to obtain time resolved emission spectra using single pulse excitation in the sub-nanosecond time frame. It has distinct advantages over the multiple excitation used by most experimenters, but the paucity of information published in the open literature of lifetime measurements by single pulse excitation presents certain difficulties in making comparative studies.

Data Reduction and Analysis

We have used two separate techniques in analyzing our experimental data. The first, the semilog plot method, is used when the excitation pulse is much shorter than the lifetime being measured. Under the experimental conditions described in this report, this occurs when lifetimes to be measured are 3 nanoseconds (3×10^{-9} sec) or longer. The technique is simple and direct. After obtaining the fluorescence curves by the method described earlier, a plot is made of the log Io/I against time. Io is the maximum fluorescence intensity, and I is the intensity at some time. The reciprocal of the slope of this plot is used to calculate τ, the lifetime of the decay. The complete technique and rationale for this method are fully described elsewhere[2]. To illustrate this method, we show in Figure 3 data obtained from a lifetime measurement on fluorescein using a picosecond excitation pulse. Curve I in Figure 3A shows the laser pulse as it is measured by the detection system. Curve II is the recorded fluorescence emission of fluorescein using the same detection system. The height of each curve is arbitrary, each being

[2] A. Pesce, C.G. Rosen and T. Pasby, Fluorescence Spectroscopy, Marcel Dekker Inc., NY, 88, 1971.

taken directly from oscilloscope traces and adjusted to fit on a single graph. Figure 3B is a semilog plot of Curve II in Figure 3A. Part of the curve is approximated by a straight line, which was fit visually for a time when the excitation pulse is in effect shut off. The slope of the line yields a value for τ of 5.88 nanoseconds. In the past, the calculation of lifetime values as short as this would have required extensive analysis using complicated apparatus and various curve matching schemes. The ability of lasers to generate ultrashort pulses has been the key to simplified nanosecond lifetime measurements. As we approach subnanosecond time frames however, the semilog plot method fails completely.

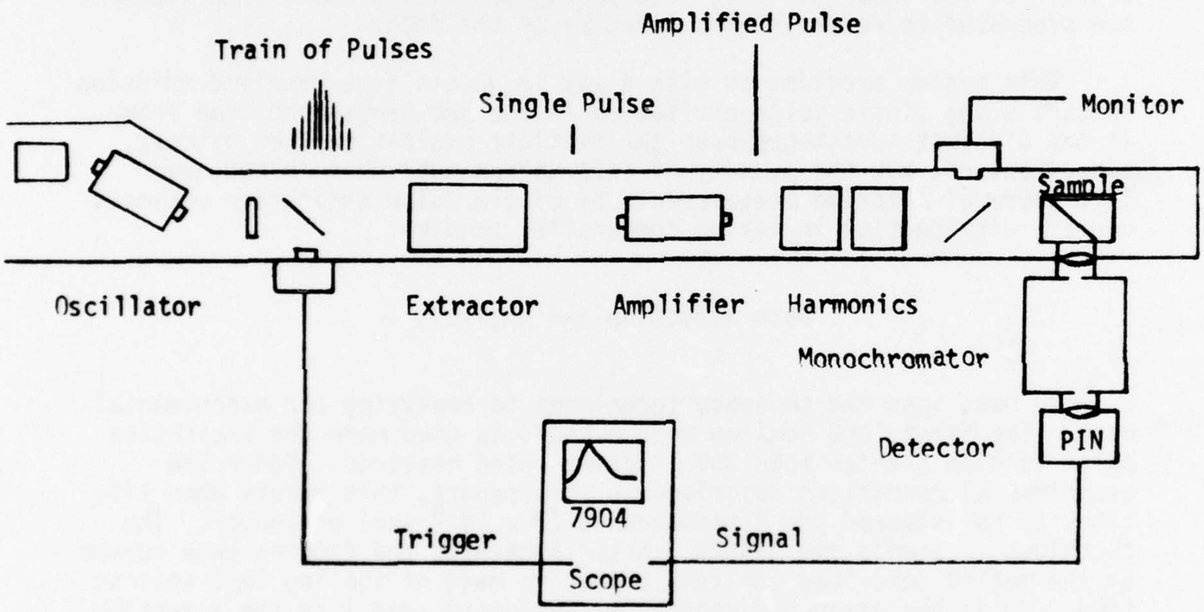

FIG. 2. EQUIPMENT FOR LIFETIME MEASUREMENTS

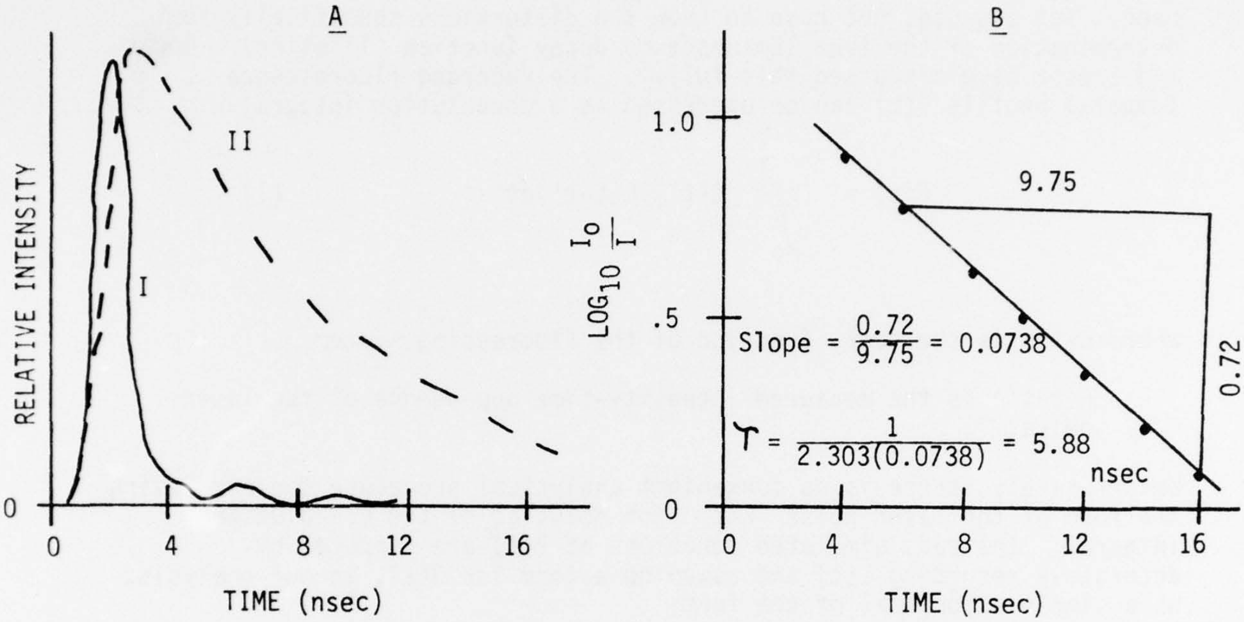

FIG. 3. A) TIME DEPENDENCE OF INTENSITY FOR EXCITATION AND EMISSION. B) SEMILOG PLOT OF CURVE II IN A).

The experimental data encountered in the study of transients in subnanosecond photophysics are in general distorted by the excitation pulse and the detector system. For picosecond pulse irradiation, only distortion by the detector system is of concern, since the optical pulse is τ 10 psec, while most lifetimes are usually greater than 100 psec. Yet one does not have to know the distortions specifically for determination of the true luminescence decay function (lifetime). Demas and Crosby have discussed this fully[3]. The recorded fluorescence temporal profile P(t) can be expressed as a convolution integral.

$$P(t) = \int_0^t G(t')\, E(t-t')dt' \qquad (1)$$

where G(t') is the decay function of the fluorescing system

E(t-t') is the measured intensity-time dependence of the laser pulse.

Unfortunately, there is no convenient analytical procedure for expressing the form of the laser pulse E(t) for solution of the convolution integral. Instead, simulated functions of P(t) are computed by accurately recording E(t) and assuming a form for G(t), in our analysis, as a simple exponental of the form

$$G(t) = e^{-t/\tau} \qquad (2)$$

The exponential decay time (lifetime) can be determined by comparing the recorded fluorescence profile with the simulated functions of P(t) until a best fit has been determined. It is the technique that has been used in the study to evaluate subnanosecond lifetimes, and with the aid of computer processing, has defined the accuracy to be $\pm$ 30 picoseconds for values down to 100 picoseconds.

Convolution Method

Collecting data is straightforward when the criteria described in the equipment section are satisfied. A schematic picture of the technique and a description of the convolution integral are shown in Figure 4. The sample is pulsed, and resulting luminescence, converted by

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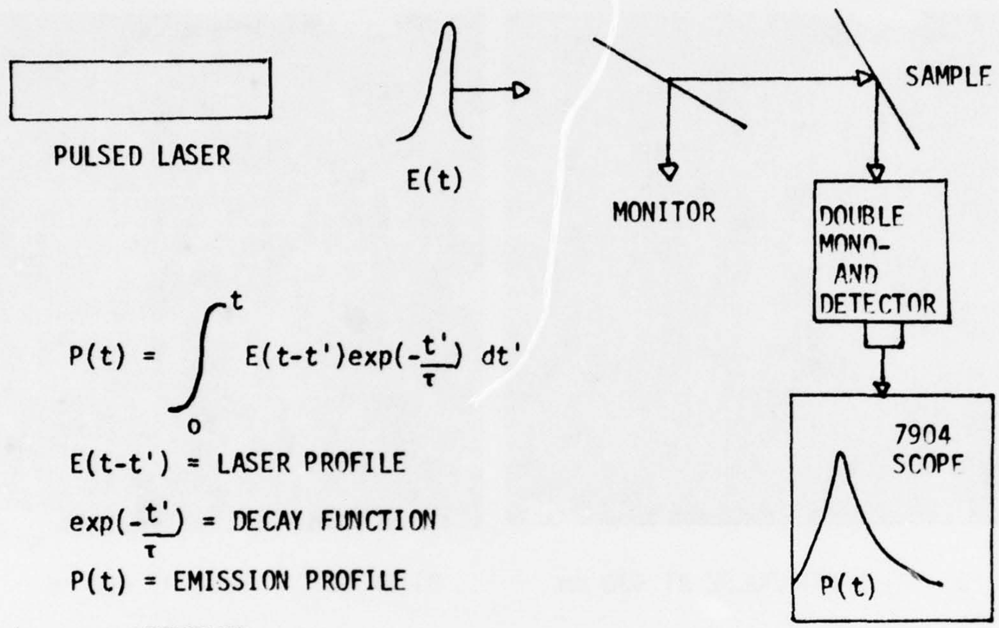
[3] J.M. Demas and G.S. Crosby; "Photoluminescence Decay Curves: An Analysis of the Effects of Flash Duration and Linear Instrumental Distortions", Anal. Chem., 42, No. 9, 1010, 1970.



$$P(t) = \int_0^t E(t-t')\exp\left(-\frac{t'}{\tau}\right) dt'$$

$E(t-t')$ = LASER PROFILE

$\exp\left(-\frac{t'}{\tau}\right)$ = DECAY FUNCTION

$P(t)$ = EMISSION PROFILE

τ = LIFETIME

FIG. 4. EMISSION LIFETIME BY CONVOLUTION

the photodetector to a corresponding voltage, is displayed and photographed on the scope. Typical data obtained in this way are shown in Figure 5.

A B

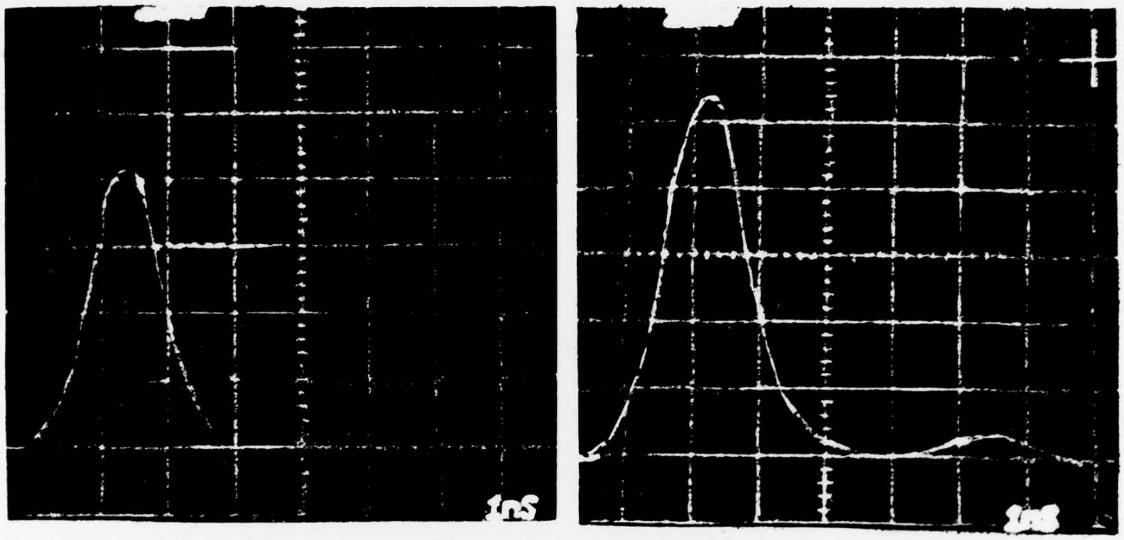


FIG. 5. A) LASER PULSE AT 530 nm B) EMISSION PULSE AT 690 nm

After these traces are obtained, they are digitized for computer processing. The general process requires that many values of τ be substituted into the exponential function of the convolution integral and associated intensity profiles of P(t) be computed. Each simulated curve is then compared to the actual emission profile, such as the one shown in Figure 5B, until the two curves are as close in shape as possible. The τ value that is used to accomplish this comparison is considered to be the lifetime for the emission. This method when first applied, was successful in determining lifetime values to within 0.50 nanosecond[4].

The computer program initially selected to process our data and perform the necessary analysis was a desk top calculator. The final program used the UNIVAC 1106 computer with refinements, such as to give a high degree of confidence in the data for subnanosecond lifetimes. The following section provides a brief history of the evolution of the final selection and the reasons for its acceptance.

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[4]R.A. Kashnow and J.A. Sousa, J. Applied Physics, 42, No. 5, April 1971.

NLCON Program

This program, NLCON, evaluates P in eq 1 from E and τ, and compares P with experimentally observed pulse profiles.

This program has been developed from a program written by Kashnow and Sousa[5]. They evaluated P from a Gaussian form of E and plotted it as a family of curves with various τ's. The experimental pulse shape was compared with those curves used as templates by a visual inspection to obtain a best fit value of τ.

Modifications have been made to accommodate any type of pulse shape E besides Gaussian, and the degree of fit between the calculated and actual luminescence pulse shapes is now expressed quantitatively in terms of root mean square (rms) values. The output consists of printouts and plots. The printout gives rms as a function of τ and d; d is a time displacement between the time coordinates of the experimental and calculated luminescence profiles. The plots are the laser profiles, observed luminescence profiles, and the best fitted calculated profiles. The printout can be used to estimate confidence limits of the lifetime values, and the plots, to note any unusualness caused particularly by errors in card punching or in digitization.

The program still has some traces of earlier versions of the program in the developmental state, but they are of no consequence in the results.

General Description:

This program reads the laser and luminescence profiles from cards, calculates and prints out rms values as a function of τ, and luminescence profiles (P) as a function of t from an optimum value of τ, τ opt. With the use of the CALCOMP plotter, the profiles of the laser and the profiles of the observed and calculated luminescence are plotted.

The mechanism of the calculations is described below.

First, a spline function routine is applied to both the laser and luminescence input profile data. The profiles are usually given in unequally spaced time intervals. Through the routine, a one-dimensional array, which represents the intensity of a profile at equally spaced time intervals, is created. The first element of the array is set to time = 0 and intensity = 0. A subsequent i-th element has the value of intensity at time = T/100 x (i - 1); i runs from 1 to 100. T, an input, is a time span set sufficiently long to contain any sample luminescence profile. If the last point of the observed luminescence profile P^+ is at a time shorter than T, then there will be empty array elements. If the last point of E is at a shorter time than T, then the rest of the

[5] R.A. Kashnow and J.A. Sousa, J. Applied Physics, 42, No. 5, April 1971.

elements are assumed to be zeroes. From the array for E, {E}, an array {P} is created by equation 1. This array also has 100 elements and is always filled. The selection of a value for τ from inputs is given in detail in the last part of this section. {P} is peak normalized and is compared with an array for peak normalized $\{P^+\}$. In principle, an i-th member of P, P_i should be compared with P^+_i because each represents the value at the same time, t = (i-1) T/100. However, in practice, P is compared with P^+_{i+d}; d is a displacement. In a time scale, this corresponds to dT/100. This displacement originates from the uncertainity in the time coordinate relationship between the oscilloscope traces of the laser and luminescence profiles. We do not know exactly where a time coordinate of one profile appears in the common coordinate. A time t for E and P may be at a time $t + \Delta t$ in P^+. Therefore, in matching P and P^+, Δt must be considered. Since two adjacent elements in an array represent intensities T/100 apart, Δt is approximated to a multiple of T/100 or dT/100. Because of this displacement, the first part of {P} or $\{P^+\}$ may not have elements to be matched in the other array. It is then assumed that these elements exist in the other array with values of zero. Also, in the tail end of {P} or $\{P^+\}$, matching elements may be absent due to either the displacement or the presence of unfilled elements in $\{P^+\}$; the calculation will not be performed on the unmatched or unfilled elements.

The rms values are calculated from the following formula:

$$\text{rms} = \sqrt{\frac{\sum_{i=d+1}^{N} (P^+_i - P_{i-d})^2 + \sum_{i=1}^{d} (P^+_i)^2}{N}} \qquad (3)$$

or

$$\sqrt{\frac{\sum_{i=d+1}^{N+d} (P^+_{i-d} - P_i)^2 + \sum_{i=1}^{d} (P_i)^2}{N+d}}$$

The former expression is used if $\{P^+\}$ precedes {P} in time, and the latter when the opposite occurs. In (3), d is a positive integer and usually has a value ranging from 0 to 10. The summations from i = 1 to i = d indicate the absence of matching elements due to the displacement. An optimum value of d is searched by a half-interval technique to minimize rms values while τ is kept constant; d is varied by intervals 4,2, and then 1 in the units of T/100. After this search, τ is decreased by an increment and the search is repeated until τ reaches a lower limit given by an initial input. All these minimized rms values associated with each τ value are compared, and the τ, which is associated with the minimum rms is τ opt. From τ opt, P (τ opt) is calculated and plotted on top of the plot of P^+ for a visual inspection.

Input and Output:

The input consists of a numerical description of the laser profiles and luminescence profiles. Each set of luminescence profile cards must be preceded by a set of its excitation laser profile cards. Each deck of laser or luminescence profile cards must have a title card in front. The program can handle any number of luminescence profiles.

The following are the explanation of the input cards. The formats for the inputs refer to those in the main program. The sequence for multiple entries on a card is the same as that given here.

<u>First Data Card</u> (FORMAT 3)

MPQ: The number of laser profiles in this data deck.

<u>A Title Card for a Laser Profile</u> (FORMAT 1)

PNAME: Title or identification.

TRANGE: Time range T which is the time span to contain the luminescence profiles. This is also the length of the X axis for the plot.

NPU: The number of cards for a laser profile. It must not exceed 49.

<u>Laser Profile Cards</u> (FORMAT 2)

PULSET, PULSEI: One value each of time and intensity of a laser profile per card. The data should not include PULSET = 0 because the program automatically adds such an element. The maximum value of PULSEI should be about, but not larger than, 100.

<u>A Number Card</u> (FORMAT 1)

NAP: The number of luminescence profiles accompanying the above laser pulse. This input device is convenient when the excitation pulse profiles are reproducible, since only one data deck of laser profile cards is needed to be punched for a number of luminescence profiles.

A Title Card for a Luminescence Profile (FORMAT 1)

ENAME: Title or identification of the profile.

TAUI: The maximum trial value of τ. The user must analyze the original data to make a rough estimate of the value of the lifetime. He then selects a range of trial values from the maximum value TAUI to the maximum value V3 (see below) which includes the estimated τ, and chooses a constant increment V2 (see below) for which this range is monotonically scanned.

NPT: The number of the following luminescence profile cards. This should not exceed 50.

WT: Weight assigned only to the P^+ elements following the maximum value in P^+. Weights are unity for other elements. If no entry is made, then all the elements in P^+ have the unit weight. This entry device is provided for the analysis of luminescence profiles much wider than the laser profile.

V2: Increment by which τ is decreased. It is always entered as a negative number. If this is 0, then a last non-zero value from an earlier title card is assigned. If this is the first luminescence title card, a zero entry will produce an uncontrolled output.

V3: The minimum trial value of τ. If this is 0, the program will interpret it as in the case of V2.

IV: The number of τ values to be tried. This is an unnecessary entry, but to prevent any runaway situation, it is entered as a safeguard. If this is 0, the program will interpret it as in the case of V2.

Luminescence Profile Cards (FORMAT 2)

ET, EI: One value each of time and intensity per card. There should be no ET = 0 as in the case for the laser profile. Since the array $\{P^+\}$ is to be normalized, there are no restrictions on the value of EI.

The data cards are stacked in the following manner:

Title cards are placed on top of their respective profile decks. If there is more than one luminescence profile with the identical excitation laser pulse profile, the data cards are simply stacked together. The number of luminescence profiles appears as NAP; the NAP

card is placed between the last card of the associated laser profile and the first luminescence title card.

If there is more than one such set of laser and luminescence profiles, one set is simply stacked on top of the other. The number of such sets appears as MPQ which is equal to the number of laser profiles in the entire data deck. One cannot omit NAP or MPQ cards even if the value is 1. No two laser pulse profiles can be stacked together without any luminescence data in between. An example of a data deck is shown in Figure 6.

The printout shows the content of input (Figure 7). The "peak value" in Figure 2 refers to the maximum value in the created array {E}, or {P}, and not to the input values.

A series of four-line paragraphs, like the one shown in Figure 8, shows rms values as a function of τ. The third line in each paragraph shows the iterative path of the search of optimum d with its associated rms value. The value of d is not given explicitly; it is shown as time displacement between the two peaks of P and P^+. These peaks are used as the time coordinate reference points instead of the origins. Similarly, the optimum time displacement, instead of optimum d, is given in the last line. If the number of iteration exceeds eight, then the extension of the line appears as the fourth line.

Upon completion of the rms calculation for the entire range of τ values from TAUI to V3, the τ opt with its rms values are given. Finally a table is printed showing every fifth element of the arrays {E},{P (τ opt)}, and {P^+}, starting from the first element (Figure 9). The table does not show the time displaced relationship between {P} and {P^+}. The reason for showing just every fifth element is for the sake of brevity only.

Example:

The example presented here is an actual case of luminescence lifetime analysis for an acid blue dye dissolved in dimethylformamide. The laser profile and the luminescence profile were digitized by the use of a Hewlett Packard digitizer, coupled to H-P 9820 calculator. The printout from the calculator was punched onto cards manually. Inputs are shown in Figure 6.

The first output LASPUL 1 shows the input tables for the laser profile except for the 0 - 0 values (Figure 7). The second table FL 13G is for the luminescence profile. A series of four-line paragraphs appear immediately after the input tables. Figure 8 shows only the end and a middle section of the series for brevity.

```
 1
LASPUL 1 11476                    5.000      22
   .348      2.542
   .646      8.475
   .796     15.254
   .994     27.966
  1.144     37.288
  1.243     50.000
  1.343     57.627
  1.442     64.407
  1.541     67.797
  1.641     70.339
  1.790     70.339
  1.939     65.254
  2.088     55.932
  2.188     44.915
  2.337     33.898
  2.436     23.729
  2.635     14.407
  2.834      7.627
  2.983      4.237
  3.282      1.695
  3.680      1.695
  3.928      1.695
 1
FL 13G 111276                      .600      27      -.025      .1       21
   .201      0.000
   .553      1.653
   .906      5.785
  1.057     11.570
  1.208     19.835
  1.409     28.926
  1.459     37.190
  1.610     50.413
  1.711     64.463
  1.811     72.727
  1.912     80.992
  2.013     85.950
  2.164     89.256
  2.314     89.256
  2.465     85.950
  2.516     80.992
  2.566     73.554
  2.767     58.678
  2.918     43.802
  3.119     33.058
  3.321     20.661
  3.522     14.050
  3.673      9.917
  3.925      6.612
  4.126      4.959
  4.377      3.306
  4.629      2.479
```

FIG. 6. EXAMPLE OF A DATA DECK

```
EXCITATION PULSE ID - LASPUL 1 11476
     TIME       INTENSITY
     .000          .000
     .348         2.542
     .646         8.475
     .796        15.254
     .994        27.966
    1.144        37.288
    1.243        50.000
    1.343        57.627
    1.442        64.407
    1.541        67.797
    1.641        70.339
    1.790        70.339
    1.939        65.254
    2.088        55.932
    2.188        44.915
    2.337        33.898
    2.436        23.729
    2.635        14.407
    2.834         7.627
    2.983         4.237
    3.282         1.695
    3.680         1.695
    3.928         1.695
PEAK VALUE OF PROFILE    =        .71019+02 AT TIME  =    1.70
EMISSION OF FL 13G 111276
     TIME       INTENSITY
     .000          .000
     .201          .000
     .553         1.653
     .906         5.785
    1.057        11.570
    1.208        19.835
    1.409        28.926
    1.459        37.190
    1.610        50.413
    1.711        64.463
    1.811        72.727
    1.912        80.992
    2.013        85.950
    2.164        89.256
    2.314        89.256
    2.465        85.950
    2.516        80.992
    2.566        73.554
    2.767        58.678
    2.918        43.802
    3.119        33.058
    3.321        20.661
    3.522        14.050
    3.673         9.917
    3.925         6.612
    4.126         4.959
    4.377         3.306
    4.629         2.479
PEAK VALUE OF PROFILE    =        .89437+02 AT TIME  =    2.20
```

FIG. 7. EXAMPLE OF A PRINTOUT OF A CONTENT OF INPUT

```
        LET    TAU  =  .600
  PEAK VALUE OF PROFILE = .94910+03 AT TIME = 2.10
  .100 5.177   .300 11.621   .000 7.815   .150 5.632   .050 6.055
SUB DT - WITH TIME DISPLACEMENT = .100 AND RMS = 5.177 AFTER ITERATION NO. 5

        LET    TAU  =  .575
  PEAK VALUE OF PROFILE = .92377+03 AT TIME = 2.10
  .300 10.817   -.100 12.647   .200 6.339   .050 6.044   .150 4.899
SUB DT - WITH TIME DISPLACEMENT = .100 AND RMS = 4.777 AFTER ITERATION NO. 5

        LET    TAU  =  .450
  PEAK VALUE OF PROFILE = .78622+03 AT TIME = 2.05
  .400 11.848   .000 10.765   .300 6.508   .150 3.119   .250 3.991
SUB DT - WITH TIME DISPLACEMENT = .200 AND RMS = 2.237 AFTER ITERATION NO. 5

        LET    TAU  =  .425
  PEAK VALUE OF PROFILE = .75547+03 AT TIME = 2.00
  .400 11.011   .000 11.571   .300 5.619   .150 3.594   .250 3.104
SUB DT - WITH TIME DISPLACEMENT = .200 AND RMS = 1.840 AFTER ITERATION NO. 5

        LET    TAU  =  .400
  PEAK VALUE OF PROFILE = .72414+03 AT TIME = 2.00
  .400 10.161   .000 12.442   .300 4.740   .150 4.304   .250 2.301
SUB DT - WITH TIME DISPLACEMENT = .200 AND RMS = 1.990 AFTER ITERATION NO. 5

        LET    TAU  =  .375
  PEAK VALUE OF PROFILE = .69136+03 AT TIME = 2.00
  .400 9.309   .000 13.379   .300 3.905   .150 5.171   .250 1.753   .300 3.905
SUB DT - WITH TIME DISPLACEMENT = .250 AND RMS = 1.753 AFTER ITERATION NO. 6

        LET    TAU  =  .350
  PEAK VALUE OF PROFILE = .65708+03 AT TIME = 2.00
  .450 11.201   .050 11.641   .350 5.739   .200 3.518   .300 3.167
SUB DT - WITH TIME DISPLACEMENT = .250 AND RMS = 1.768 AFTER ITERATION NO. 5

        LET    TAU  =  .150
  PEAK VALUE OF PROFILE = .34136+03 AT TIME = 1.85
  .600 12.206   .200 13.212   .500 7.427   .350 6.204   .450 5.702
SUB DT - WITH TIME DISPLACEMENT = .400 AND RMS = 5.185 AFTER ITERATION NO. 5

        LET    TAU  =  .125
  PEAK VALUE OF PROFILE = .29659+03 AT TIME = 1.80
  .600 11.286   .200 14.566   .500 6.886   .350 7.306   .450 5.668   .500 6.886
SUB DT - WITH TIME DISPLACEMENT = .450 AND RMS = 5.668 AFTER ITERATION NO. 6
```

FIG. 8. EXAMPLE OF A PRINTOUT OF RMS VALUES AS A FUNCTION OF τ

NORMALIZED VALUES AT TAU = .375 WITH RMS = 1.753

TIME	PULSE INTENSITY	EMISSION INTENSITY	CALCULATED INTENSITY
.00	.000	.000	.000
.25	2.018	.122	.593
.50	6.736	1.502	3.066
.75	17.931	3.457	9.037
1.00	39.795	9.840	22.809
1.25	71.440	22.975	44.117
1.50	93.903	46.862	71.897
1.75	99.840	76.343	92.615
2.00	87.867	95.584	100.000
2.25	56.496	99.979	89.509
2.50	27.037	92.712	67.008
2.75	14.721	66.976	45.029
3.00	5.585	43.013	27.720
3.25	2.526	27.793	16.082
3.50	2.179	16.363	9.492
3.75	2.413	9.462	6.200
4.00	.000	6.689	3.885
4.25	.000	4.553	1.995
4.50	.000	3.053	1.024
4.75	.000	.000	.526

END OF PROGRAM

FIG. 9. EXAMPLE OF A PRINTOUT OF AN OBSERVED AND A CALCULATED LUMINESCENCE PROFILE

The third line in each paragraph shows the course of the program searching for the optimum time displacement. The displacement and rms values are printed in pairs in order of trials. The first paragraph in Figure 8 is for τ = 0.600, which is the first trial value of τ, INTAU. For this τ, the first trial value of time displacement is the difference in peak positions of P and P^+, which is -0.1. This value is not printed out, but is stored for the comparison. The second trial value of the time displacement is -0.1 + dT/100 = 0.1, in which d = 4 and T = 5.0. This is printed out as the first number in the third line with a rms value.

The third trial value is 0.1 + dT/100 = 0.3 because the program recognized that the rms value decreased in going from the displacement of -0.1 to 0.1. The fourth value is 0.1 + (-2)T/100 = 0 because the rms value has become larger in the continuous increase of the displacement from 0.1 to 0.3. The increment is halved and the direction of the search reversed. Similar processes continue, as are shown in the printout.

The second paragraph in Figure 8 is for τ = 0.575. The first trial value of the time displacement is 0.1 which is adopted from the value printed in the last line of the preceeding paragraph. This trial value is not printed in the third line of this paragraph, but is stored as in the case of the first paragraph; it happens to appear as the optimum value in the last line of the paragraph.

The middle section of the figure illustrates how rms values behave near τ opt. The rms value is minimum when τ = 0.375. By inspecting this section, one recognizes that rms values do not appear to be a monotonic function of τ. This occurs because the profile is treated as an array of elements, not as a continuous function, and the time displacement is made in incremental jumps.

The final part of the printout from a run is shown in Figure 9.

The plots from the CALCOMP are shown in Figures 10 and 11. Figure 10 is the normalized observed and normalized calculated luminescence profiles. Figure 11 shows the laser and luminescence profiles. They are not normalized. The star marks indicate the input points. The line is drawn by the application of a spline function.

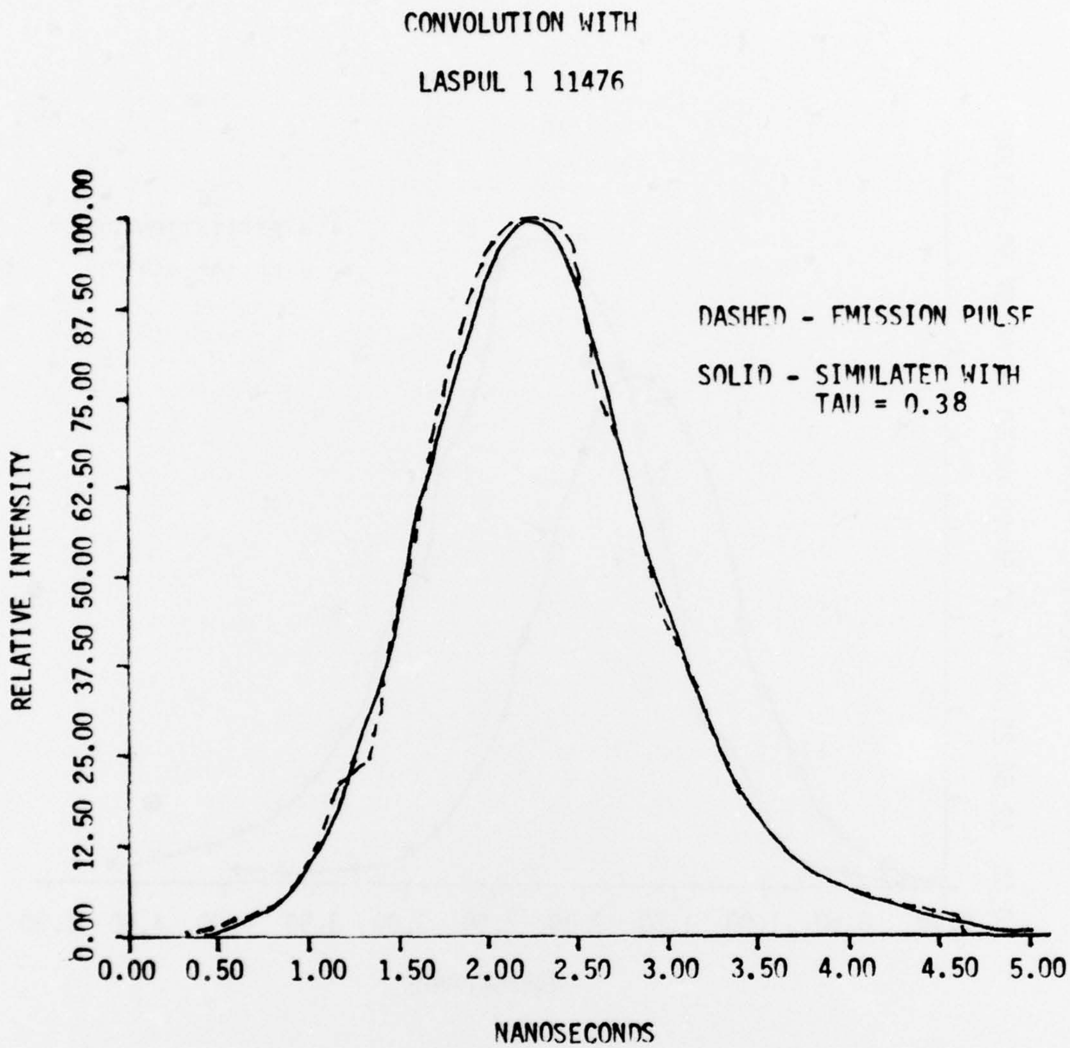

FIG. 10. EXAMPLE OF A CALCOMP PLOT OF AN OBSERVED AND A CALCULATED LUMINESCENCE PROFILE

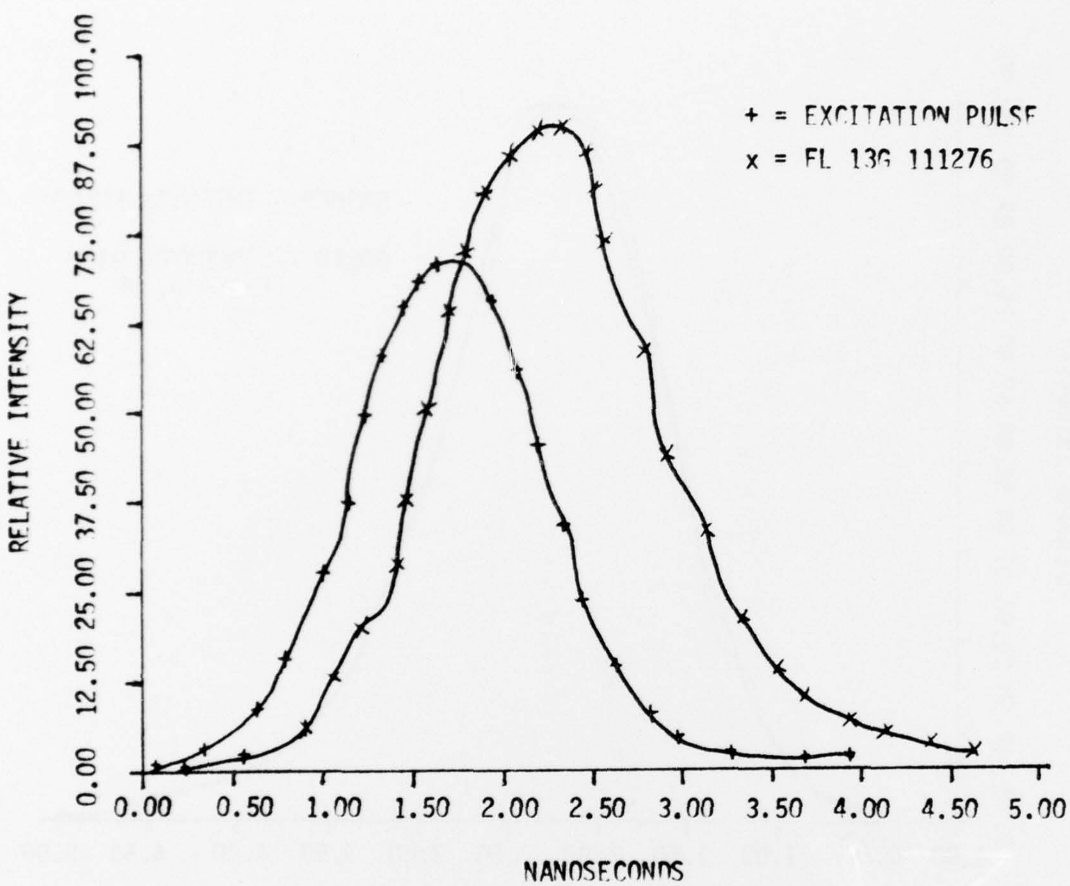

FIG. 11. EXAMPLE OF A CALCOMP PLOT OF A LASER AND AN OBSERVED LUMINESCENCE PROFILE

APPENDIX

PROGRAM PRINTOUT

Appendix

Program Printout

```
C   *****CONVOLUTION PROGRAM******
C    *** INPUT CARDS****
C      MPQ -- I3  NO. OF PULSE SETS
C    ***DATA CONCERNING EXCITATION (LASER) PULSE ***
C        TITLE CARD FOR LASER PROFILE
C      PULSE NAME - A30, TIME RANGE - F10,  NPU - I5  NO. OF PTS IN PULSE
C       TIME, INTENSITY DATA PAIRS 2F10
C     DATA , LUMINESCENCE ASSOCIATED WITH THE ABOVE EXCITATION PULSE
C      **NAP, I3  ---NO OF EMISSIONS ASSOCIATED WITH PULSE**
C   ***EMISSION DESCRIPTION****
C        TITLE CARD FOR LUMINESCENCE PROFILE
C         PROFILE
      REAL INTAUC(102),INTAU2(102)
      DIMENSION PNAME(5), ENAME(5), ARRAY(102), P(102), E(102),AINTAU(10
     62),PULSET(52),ET(52),EI(52),D(2)
      COMMON DIV,NT,NE,PULSEI(52),V(5), C(147),W(147),TEMAX,WT,T,KOUNT
    1 FORMAT (5A6,F10.5,I5,F4.2,6X,2F6.0,I5 )
    2 FORMAT(2F10.3)
    3 FORMAT(I3)
    4 FORMAT (6X,4HTIME,6X,9HINTENSITY)
    5 FORMAT (F10.3,F15.3)
    6 FORMAT ('1EXCITATION PULSE ID - ',5A6)
    7 FORMAT('1EMISSION OF ',5A6)
   15 FORMAT(' END OF PROGRAM')
C    ****INITIALIZE SPLINE***
      DATA D(2),PULSEI(1),PULSET(1),ET(1),EI(1),D(1)/6*0./
C   ***INITIALIZE PLOTTER****
      DATA P(101),E(101),INTAUC(101)/3*0.0/
      DATA P(102),E(102),INTAUC(102)/3*12.5/
      CALL PLOTS(DUM,DUMY,14)
      CALL FACTOR(0.5)
      CALL PLOT (0.0,-36.,-3)
C     *** INPUT NO OF PULSES TO BE PROCESSED ***
      READ(5,3)MPQ
      DO 1000  KQ=1,MPQ
      N = 50
      READ (5,1) PNAME, TRANGE, NPU
      IF (NPU.GT.0) N=NPU+1
      DO 100  I=2,N
      READ (5,2) PULSET(I), PULSEI(I)
      NP=I
      IF (I.LT.4) GO TO 100
      IF(PULSET(I).EQ.0.0.AND.PULSEI(I).EQ.0.0) GOTO 101
  100 CONTINUE
  101 CONTINUE
```

```
C
      CALL ORDER (PULSET,PULSEI,NP)
      CALL ZERO(P)
C   ***CALCULATE SPLINE COEFFICIENTS FOR PULSE***
      CALL SPLN1 (NP,PULSET,PULSEI,1,D,C,W)
      DIV=TRANGE/100.
      WRITE (6,6)(PNAME(I), I=1,5)
      WRITE (6,4)
      WRITE (6,5) (PULSET(I),PULSEI(I), I=1,NP)
C *** GENERATE ARRAY ****
      DO 21 I=1,100
   21 ARRAY(I)=DIV*FLOAT(I-1)
C   ***CALCULATE PULSE SPLINE AT INCREMENTS***
      P(1) = 0.0
      TD = 0.0
      DO 200 I = 2,100
      TD = TD + DIV
      IF (TD.GE.PULSET(NP)) GO TO 201
      V(1) = TD
      CALL SPLN2 (NP,PULSET,PULSEI,C,V)
  200 P(I) = V(2)
  201 CONTINUE
C
      CALL NORM (P,TPMAX)
C   ***READ NO OF EMISSIONS WITH PREVIOUS PULSE****
      READ (5,3) NAP
      DO 1000 MKP=1,NAP
      N = 50
C   ***READ EMISSION DESCRIPTION***
      WT= 0.0
       READ(5,1) ENAME,TAUI,NPT,WT,V2,V3,IV
      KOUNT=0
      IF (V2.NE.0.) VAL2=V2
      IF (V3.NE.0.) VAL3=V3
      IF(IV.NE.0) IVAL=IV
      IF(NPT.GT.0) N=NPT+1
      WRITE (6,7) (ENAME(I), I=1,5)
   33 FORMAT(1H+,T45,'WEIGHTED AFTER THE EMISSION PEAK BY ',F4.1)
      IF(WT.GT. 0.0) WRITE(6,33) WT
      DO 102 I = 2,N
      READ(5,2) ET(I),EI(I)
      NE=I
      IF(I.LT.4) GO TO 102
      IF (ET(I).EQ.0.0.AND.EI(I).EQ.0.0) GOTO 103
  102 CONTINUE
  103 CONTINUE
      CALL ORDER (ET,EI,NE)
C   ***CALCULATE EMESSION SPLINE COEFFICIENTS***
      CALL SPLN1(NE,ET,EI,1,D,C,W)
      CALL ZERO (E)
```

```
      WRITE (6,4)
      WRITE (6,5) (ET(I),EI(I), I=1,NE)
C   ***CALCULATE SPLINE FOR EMISSION AT INCREMENTS***
      E(1) = 0.0
      TD = 0.0
      DO 204 I = 2,100
      TD = TD+DIV
      IF(TD.GE.ET(NE)) GOTO 203
      V(1) = TD
      CALL SPLN2 (NE,ET,EI,C,V)
  204 E(I) = V(2)
  203 CONTINUE
      CALL NORM (E,TEMAX)
C   ***PLOT PULES AND EMISSION CURVE ON CALCOMP***
C   ***SET ORIGIN****
      CALL PLOT (0.0,3.2,-3)
      CALL SCALE(ARRAY,10.,100,1)
      PULSET(NP+1)=ARRAY(101)
      PULSET(NP+2)=ARRAY(102)
      PULSEI(NP+1)=0.0
      EI(NE+1)=0.0
      PULSEI(NP+2)=12.5
      EI(NE+2)=12.5
      CALL AXIS(0.0,0.0,11HNANOSECONDS,-11,10.,0.,ARRAY(101),ARRAY(102))
      CALL AXIS(0.0,0.0,18HRELATIVE INTENSITY,18,8.,90.,0.0,12.5)
C******PLOT INPUT DATA*****
    ***PULSE DATA******
      CALL FLINE (PULSET,PULSEI,-NP,1,1,3)
      CALL SYMBOL(6.2,7.5,.14,20H+ = EXCITATION PULSE,0.,20)
      CALL NEWPEN(2)
      DO  210 I=1,NE
      IF(ET(I).GT.TRANGE) GOTO 210
      XX=ET(I)/ARRAY(102)
      YY=EI(I)/12.5
      CALL SYMBOL (XX,YY,0.07,4,0.0,-1)
  210 CONTINUE
      CALL PLOT(0.0,0.0,3)
      DO 220 I=1,100
      YY=T*E(I)/1250.
      XX=ARRAY(I)/ARRAY(102)
  220 CALL PLOT(XX,YY,2)
      CALL SYMBOL(6.2,7.2,0.14,4HX = ,0.0,4)
      CALL SYMBOL (999.,999.,0.14, ENAME,0.0,30)
      CALL NEWPEN(1)
C
C   CALCULATION OF RMS AND VARIATION OF LIFETIME BY INCREMENT VAL2
       PRINT  9
      IT = 0
      TAUC=TAUI
       TAUMIN = TAUI
```

```
      CALL SIME(P,INTAUC,TAUC)
      CALL NORM(INTAUC,TTAMAX)
      CALL DT(INTAUC,TTAMAX,RMSC,TDISC,E)
       KOUNT = 3
       TDIS2=TDISC
      TINC=VAL2
      TAU2=TAUC
  600 TAU2=TAU2+TINC
C    *** TO QUIT ITERATION ***
      IF (TAU2.LE.VAL3) GOTO 605
      IT=IT+1
      IF (IT.GT.IVAL) GOTO 605
      CALL SIME(P,INTAU2,TAU2)
      CALL NORM(INTAU2,TTAMA2)
      KOUNT=KOUNT+1
      CALL DT(INTAU2,TTAMA2,RMS2,TDIS2,E)
    9 FORMAT (/15X, 10H----------)
C   ***PICK THE TAU FOR RMSMIN AND PRINT AND STORE TAU RMS DT FOR PLOT
      IF(RMSC - RMS2) 600,600,602
  602 RMSC=RMS2
      TAUMIN=TAU2
      TDISC=TDIS2
      GOTO 600
  605 TAUC=TAUMIN
      CALL SIME(P,INTAUC,TAUC)
   11 FORMAT(///'  NORMALIZED VALUES AT TAU =',F7.3,' WITH RMS=',F7.3)
   12 FORMAT(/14X,5HPULSE,5X,8HEMISSION,3X,10HCALCULATED/
     64X,'TIME    INTENSITY   INTENSITY   INTENSITY')
   13 FORMAT (F7.2,1X, 3F12.3)
      CALL NORM(INTAUC,TTAMAX)
      PRINT 11 TAUC,RMSC
      PRINT 12
      WRITE(6,13)(ARRAY(I).P(I),E(I),INTAUC(I), I=1,100,5)
C
C    ***PLT SIMULATED BEST FITS ON CALCOMP***
      CALL PLOT(0.0,0.0,3)
      CALL PLOT(0.0,10.,-3)
      CALL AXIS(0.0,0.0,11HNANOSECONDS,-11,10.,0.,ARRAY(101),ARRAY(102))
      CALL AXIS(0.0,0.0,18HRELATIVE INTENSITY,18,8.,90.,0.0,12.5)
      CALL DASHL(ARRAY,E,100,1)
      CALL PLOT(0.0,0.0,3)
      DO 900 I=1,100
      AINTAU(I)=(ARRAY(I)+TDISC)/ARRAY(102)
      IF(AINTAU(I).LT. 0.0 .OR. AINTAU(I).GT.10.) GOTO900
      A=INTAUC(I)/12.5
      CALL PLOT(AINTAU(I),A,2)
  900 CONTINUE
      CALL SYMBOL( 6.0,7.5,0.14,23HDASHED - EMISSION PULSE,0..23)
      CALL SYMBOL(6.0,7.2,0.14,29HSOLID - SIMULATED WITH TAU =  ,0.,29)
      CALL NUMBER(999.,999.,0.14,TAUC,0.0,2)
```

```
      IF(WT.EQ. 1.0) GOTO 990
      CALL SYMBOL(7.1,6.9,0.14,20HAND TAIL WEIGHTED = ,0.0,20)
      CALL NUMBER(999.,999.,0.14,WT,0.0,1)
  990 CALL NEWPEN(1)
      CALL SYMBOL(3.,9.8,0.28,17HCONVOLUTION WITH ,0.0,17)
      CALL SYMBOL(2.0,9.0,0.28,PNAME,0.0,30)
      CALL PLOT(16.0,-36.,-3)
 1000 CONTINUE
 1001 CALL PLOT(12.0,0.0,999)
      PRINT 15
      STOP
      END


      SUBROUTINE NORM(E,TMAX)
C    ***NORMALIZE AND FIND TMAX AND IMAX OF ARRAY***
      DIMENSION E(102)
      COMMON DIV,NT,NE,PULSEI(52),V(5), C(147),W(147),TEMAX,WT,T
    1 FORMAT ('   PEAK VALUE OF PROFILE   =   ',E12.5, ' AT TIME =',
     1 F8.2)
      NT=2
      T=E(2)
      DO 10 I=3,100
      IF(T.GT.E(I)) GOTO 10
      T=E(I)
      NT=I
   10 CONTINUE
      TQ=NT-1
      TMAX=DIV*TQ
      DO 11 I=2,100
   11 E(I)=(E(I)/T)*100.
      PRINT 1, T,TMAX
      RETURN
      END


      SUBROUTINE ORDER (PT,PI,N)
      DIMENSION PT(102),PI(102)
      XTEMP=PT(1)
      YTEMP=PI(1)
      N1=N-1
      DO 10 I=1,N1
      I1=I+1
      DO 10 II=I1,N
      IF(PT(I).LT.PT(II)) GOTO010
      XTEMP=PT(II)
      PT(II)=PT(I)
      YTEMP=PI(II)
      PI(II)=PI(I)
      PI(I)=YTEMP
```

```
10 CONTINUE
   RETURN
   END


   SUBROUTINE ZERO (A)
   DIMENSION A(102)
   DO 10 I=1,100
10 A(I)=0.0
   RETURN
   END


   SUBROUTINE SIME(E,INTAU,TAUC)
   REAL INTAU
   DIMENSION INTAU(102),E(102)
   COMMON DIV,NT,NE,PULSEI(52),V(5), C(147),W(147),TEMAX,WT,T
C   ***CALCULATE SIMULATED EMISSION***
   DO 20 I=1,100
20 INTAU(I)=E(I)
   TD=0.0
   DO 10 I=1,98
   TD=TD+DIV
   F=EXP(-1.*TD/TAUC)
   I1=I+1
   DO 10 J=I1,100
   INTAU(J)=INTAU(J)+F*E(J-I)
10 CONTINUE
 1 FORMAT (//'          LET     TAU  =  ',F6.3)
   PRINT 1, TAUC
   RETURN
   END


   FUNCTION SRMS(E,INTAU,ITDIFF)
C   ***COMPUTES RMS AT DIFFERENT TIMES (TDIFF)  ***
   REAL INTAU
   DIMENSION INTAU(102),E(102)
   COMMON DIV,NT,NE,PULSEI(52),V(5), C(147),W(147),TEMAX,WT,T
   RMS=0.0
   R=0.0
   IF(WT.LE. 0.0) WT=1.0
   K=(TEMAX/DIV) + 1.0001
   IF(ITDIFF) 10,10,11
10 DO 1 I=1, 100
   IF (I+ITDIFF .LT. 1) GOTO 20
   SE =E(I+ITDIFF)
   IF (SE .EQ. 0. .AND. I .GT. 50) GOTO 3
   GOTO 21
20 SE=0.
```

```
 21 CONTINUE
    S=INTAU(I)
 26  CONTINUE
    SM= SE-S
    IF ((I+ITDIFF) .LT. K) GOTO 27
    SM=WT*SM
    R=R+(WT - 1.0)
 27 RMS = SM*SM +RMS
  1  R=R+1.
    GOTO 3
 11 DO 2 I=1, 100
    IF (I-ITDIFF .LT. 1) GOTO 30
    S= INTAU(I-ITDIFF)
    GOTO 31
 30  S=0.
31  CONTINUE
    SE = E(I)
    IF (SE .EQ. 0. .AND. I .GT. 50) GOTO 3
 36 CONTINUE
    SM = SE -S
    IF (I .LT. K) GOTO 37
    SM = WT*SM
    R = R+(WT-1.0)
 37  RMS = SM*SM + RMS
  2 R = R+1.
  3 SRMS = SQRT(RMS/R)
    RETURN
    END


    SUBROUTINE DT(INTAU,TTAMAX,RMSX,TDISX,E)
    REAL INTAU
    DIMENSION INTAU(102),E(102)
     DIMENSION AID(12),BID(12)
    COMMON DIV,NT,NE,PULSEI(52),V(5), C(147),W(147),TEMAX,WT,T,KOUNT
    IC=0
     C=0.8
    IF (KOUNT.GT.2) GOTO 99
    TDISX=TTAMAX-TEMAX
 99 ITDIS = 1.0001*TDISX/DIV
    RMS1=SRMS(E,INTAU,ITDIS)
700 ITDIS2=ITDIS+IFIX(5.0*C+0.6*(ABS(C)/C))
    IC=1+IC
    IF (IC .GT. 12) GOTO 703
    RMS2=SRMS(E,INTAU,ITDIS2)
  3 FORMAT (2X,8(F9.3,F7.3))
     AID(IC) = DIV*FLOAT(ITDIS2)
     BID(IC) = RMS2
    IF(RMS1-RMS2) 701,702,702
701 C=-C
```

```
      IF(IC.GT.1) C=C/2.
      IF (ABS(C).LT. 0.09) GOTO 704
      GOTO 700
  702 ITDIS=ITDIS2
      RMS1=RMS2
      IF(ABS(ITDIS2-ITDIS).EQ.1) GOTO 704
      GOTO 700
  703 PRINT 2
    2 FORMAT ('  **AFTER GREATER THAN TWELVE ITERATIONS***')
  704 TDISX=DIV*FLOAT(ITDIS)
       WRITE(6,3) (AID(J),BID(J),J=1,IC)
      RMSX=RMS1
      WRITE(6,11) TDISX,RMSX,IC
   11 FORMAT('  SUB DT - WITH TIME DISPLACEMENT =',F7.3,' AND RMS = ',
     6F7.3,' AFTER ITERATION NO.',I3)
      RETURN
      END
```

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